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QUARTERLY REPORT FOR THE PERIOD 4/1/94 TO 7/30/94

NANOSTRUCTURED BEARING ALLOY STUDIES
[ONR N00014-94-1-0579]

SUBMITTED TO

OFFICE OF NAVAL RESEARCH
MATERIALS SCIENCE DIVISION
ARLINGTON VA

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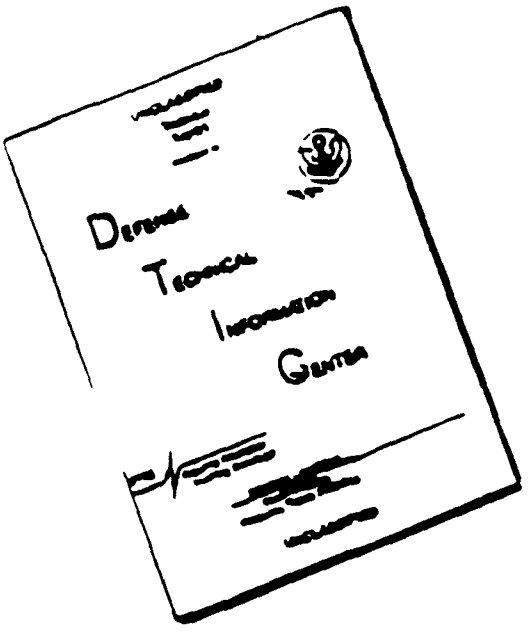

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1. SYNTHESIS OF M50 STEEL
University of Connecticut(K. Gonsalves PI)

A variation of the method reported previously for the synthesis of *M50 type steel* (*Nanostructured Mater.* 4(2), 139-147, 1994) was made. Iron pentacarbonyl(*liquid*) was mixed with vanadium carbonyl(*solid*) , bis(ethylbenzene)chromium(*liquid*) and bis(ethylbenzene)molybdenum(*liquid*) in dry decalin. The mixture was maintained under an inert argon atmosphere and stirred at 85-90 ^{o}C for 24 hrs and then at 150 ^{o}C for another 12 hrs. A black solid precipitated and the reaction was concluded at the end of approx. 36 hrs when a clear top layer of the solvent resulted. The solvent was then distilled off under reduced pressure, and the black shiny solid maintained under an argon atmosphere, was sealed and delivered to *Pratt & Whitney* for consolidation. The powders were provided to *P&W* without any organic protective coating. This is a <u>significant departure</u> from the previously reported synthesis and consolidation. Two batches of 25g were prepared by the above method and scale -up to 100 g batches is feasible.

These powders are being analyzed for their respective elemental composition.

2. PROCESSING[consolidation]
Pratt & Whitney(C.C. Law PI)

The first batch of 25 grams of nanostructured powder was received on June 21, 1994. The powder, <u>*which was not coated*</u>, was kept in a glass reactor and protected from oxidation with purified argon. Two vacuum hot press trials have been conducted on this batch. The experimental procedures used and results are described as follows:

Experimental

<u>Transfer of powder to the die:</u>

In the first hot trial about 13 grams of powder was removed from the glass reactor under an argon atmosphere in a glove box. It was observed that the powder particles tended to agglomerate into flakes with shiny surfaces and loosely packed clusters with irregular shapes. The agglomerated powder was easily fragmented using a mortar and pestle. After fragmentation the powder was transferred to a glass beaker for outgassing. The outgassing was conducted in

the glove box and involved heating the powder to about 230 °C in a vacuum for 1.5 hours. The outgassed powder was then transferred to a steel die with 12.7 mm diameter cavity under an argon atmosphere. The powder in the die was densified by tapping the die wall and the alumina plunger with a mallet. To protect the powder in the die from oxidation during transfer to the hot press, the filled die was enclosed and sealed in a stainless steel bag while still under an argon atmosphere in the glove box.

Vacuum Hot Pressing:

The die, together with the stainless steel enclosure, was installed in the hot press. After evacuation of the hot press, the stainless steel was punctured by downward movement of the top load ram to which two spears were affixed. The die was then heated to 650 °C using graphite heating elements. The vacuum in the hot press during heating was in the low 10^{-5} Torr. Upon reaching 650 °C, an initial pressure of 275 MPa was applied to the powder. The displacement of the load ram was monitored during the load application. The pressure was increased by 35 MPa increments whenever the load ram displacement rate was below 0.2 micrometer per second. The consolidation experiment was terminated when a maximum pressure of 450 MPa was reached, which is near the stress limit for the steel die used.

The procedures used for the second hot press trial were similar to those described, except that the initial outgassing was conducted in the hot press rather in the glove box, and the consolidation was conducted at a lower stress and higher temperature, 275 MPa and 800 °C.

Results and Discussion

By weighing the powder before and after heating for 1.5 hours at 230 °C in the glove box, a weight reduction of 5.55 % was observed. The major contributor to the weight change is outgassing. However, some oxidation of the powders may also have occurred during the outgassing which would increase the weight of the powder. The oxygen content of the initial powder and the consolidated material will be determined.

Inspection of the die after both hot press trials showed obvious deformation of the die during the powder consolidation. The deformation was especially severe in the second trial in which a

higher consolidation temperature was used. The die deformation resulted in incomplete consolidation of the powder in both trials. The dimensions of the first compact was about 13.2 mm in diameter, 11.7 mm high and the density was measured to be 73.2% of the conventional M50 steel. Specimens from the first compact are being prepared for microstructural, phase, and crystalline size characterization and phase transformation temperature measurement.

As a result of the severe deformation of the die, some of the material in the second consolidation was extruded to fill the gap between the alumina die and the bulged die cavity. The remaining material was embedded between the alumina die and steel support at the bottom. Rather limited amount of material from this consolidation is available for study.

More temperature resistant dies made of the molybdenum alloy TZM and alumina are being procured and will be used for the consolidation of the second batch of nanostuctured M50 powder.

3. CHARACTERIZATION
NAVAL RESEARCH LAB(G. M. CHOW PI)

1. The M50 powder(synthesized 6/22/91), sample M50-1, was received on 7/19/94. The black powder was very magnetic and appeared to be agglomerated when viewed in the HRTEM.

2. HRTEM results showed that the particles were amphorous with some very small crystalline domains.

3. XRD showed that they were X-ray amphorous. There was a very broad peak at low angles(around 20 degrees). Perhaps it is due to the organics.

Work plan on this sample:
use image processing to analyze the HRTEM image.

4. HRTEM[preliminary results on a consolidated sample prepared 7/93]
(in collaboration with Prof. M. J. Yacaman UNAM & K. Gonsalves PI)

Experimental Procedures

The observation of these M50 specimens were carried out on a high resolution transmission electron microscope(JOEL 400EX). The specimens were initially polished with a dimple grinder where the final specimen thickness obtained was of the order 30 micrometers. Subsequently, these specimens were finally prepared using an ion beam instrument. The acceleration voltage of the ion machine was approximately 5000 volts and the gas was argon.

RESULTS AND DISCUSSION

TEM OBSERVATIONS

These observations were carried out on a transmission electron microscope (TEM) using an acceleration voltage of 400 kV. This instrument has a point to point resolution of approximately 1.7 A. Fig. 1 shows a general view of the M50 specimen. This image was taken under dark field conditions (the directly transmitted beam is not allowed to pass through the objective aperture to form the final image). This image shows a large number of small crystalline regions with different types of lattice fringes (need to use a magnifier). This suggests crystalline grains at different orientations(shown in the arrows). Under these conditions it is very difficult to find out which of these crystalline regions corresponds to carbides or to the iron compounds. However, in this image there are some regions which seems to be amorphorous (shown in double arrows). In Fig. 2 two different types of lattice fringes are shown. The square array of dots give rise to an interplanar distance of approximately 2.88 A with a crystalline orientation of the (100) type. This distance is similiar to the interplanar distance obtained in the alpha-iron which is 2.88 A. In the region pointed by the arrows there is a new set of fringes with a large interplanar distance. These fringes correspond to Moire fringes obtained when two crystalline regions are stacked one on top of the other. This is probably a carbide on the crystalline alpha-iron. Fig. 3 on the other hand, shows two kinds of high resolution features. Firstly, there is a set of weak lattices fringes whcih run along most of the specimen. However, there is also a hexagonal array of dots with dot to dot distance of approximately d=3.02 A (with arrows in the figure). This distance is in closed agreement with the hexagonal

alpha Mo_2C whose d(100)=3.01 A. Therefore, these regions of hexagonal arrangements of dots are probably molybdenum carbides and the weak parallel fringes will correspond to the (matrix) alpha-Fe material. There are also small particles with interplanar distances which are close to the vanadium carbide distances. This is illustated in figure 4, where the region limited by arrows shows a small particle with interplanar distance of the order of 2.88 A. The size of the particle is approximately 24 nm. The measured interplanar distance (2.88) is close to the d(100)=2.91 A of the hexagonal V_4C_3 (Epsilon) phase.

The other important characteristic to be mentioned is the presence of amorphorous regions in the M50 specimen. This is clearly illustrated in Fig. 5 where a small structurally unknown particle surrounded by amorphorous material can clearly be seen. Finally, there are some areas in the M50 specimen which show fringes very similiar to those obtained from crystalline graphite.

The *main conclusions* of the high resolution TEM observations are as follows:

a) There are three different type of materials regions in the specimen. Amorphous areas, crystalline large grains usually 100 nm or larger or smaller crystalline regions (10-25 nm), which is usually found inside the grains or close to the grain boundaries.
b) There are large regions in the specimen with lattice parameter similar to the parameter in the alpha-Fe structure.
c) Two different carbides have been obtained based on the interplanar distances and the value of the angles in the hexagonal array of dots shown in the high resolution images. These carbides are of the vanadium carbide and molybdenum carbide types.
d) There are some graphitized zones in the specimen M50.

Fig. 2

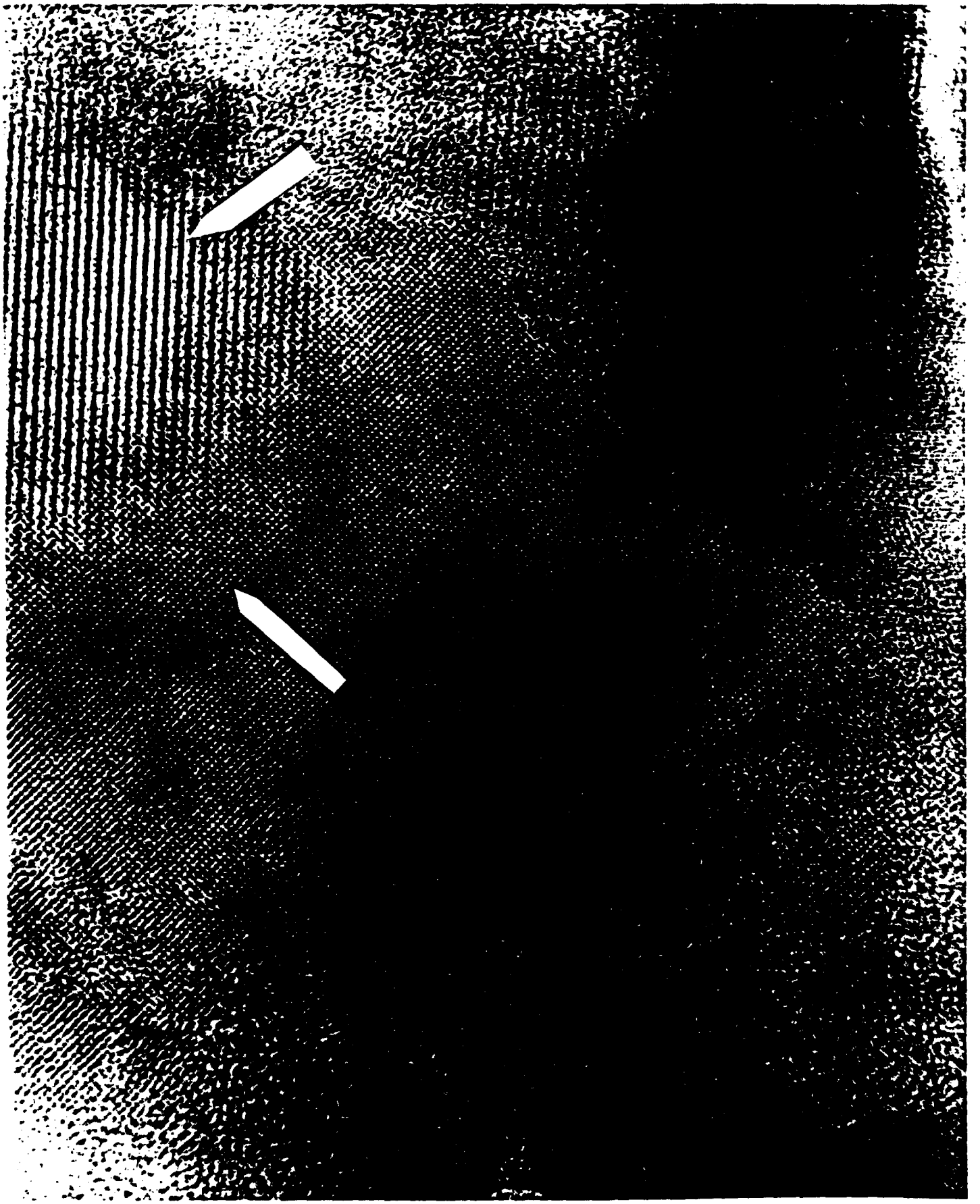

Fig. 3

Fig. 4

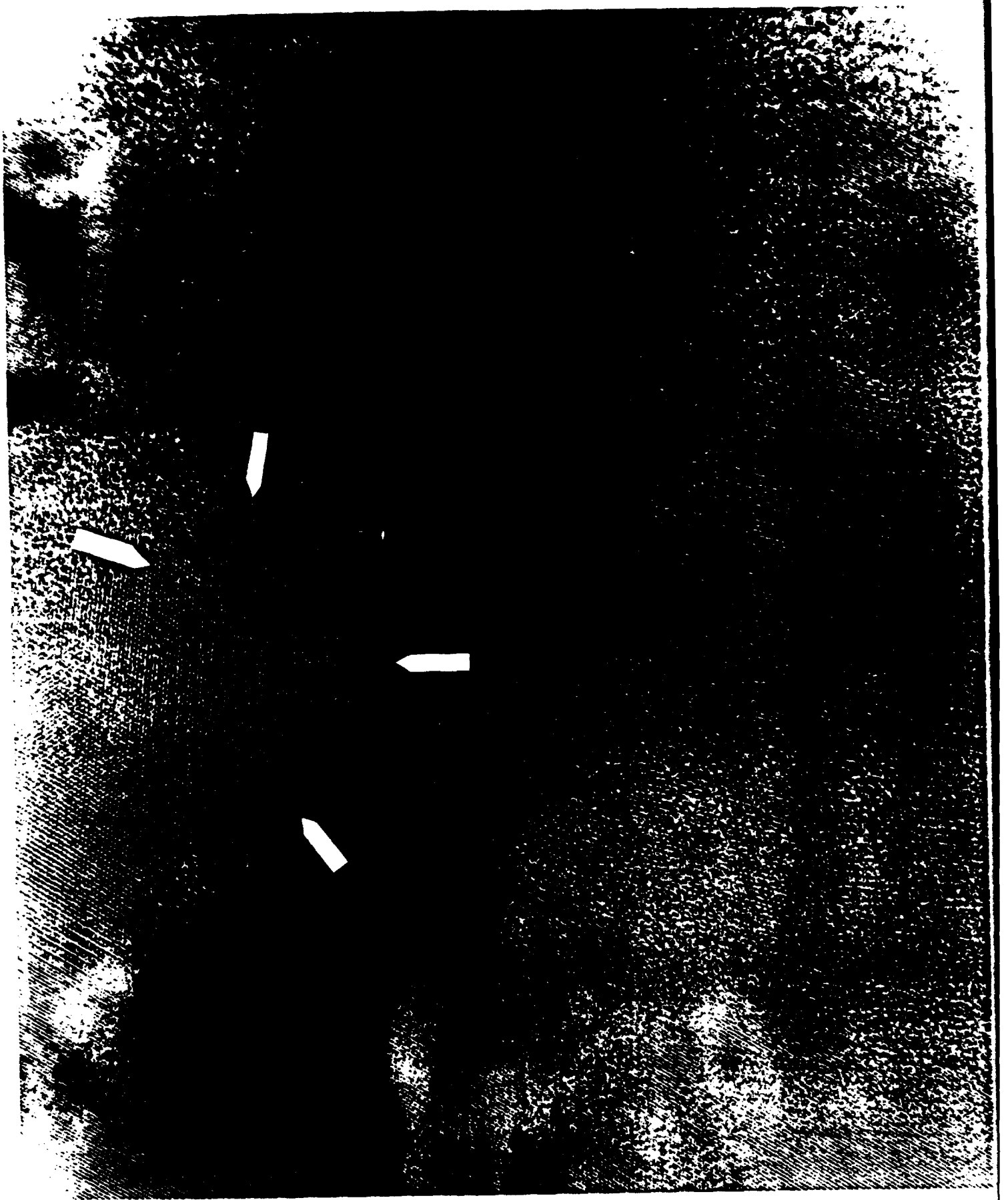

Fig. 5